Ionic Size in Relation to Molecular Physics, together with a New Law Relating to the Heats of Formation of Solid, Liquid, and Ionic Molecules.

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1. *Introduction.*—The greater part of this communication is concerned with obtaining the volumes and densities of the ions and ionic nuclei of three salts (KCl, NaCl, LiCl) from conductivity, viscosity, and freezing-point data, a process which is of limited interest and is therefore reserved for the later sections of this communication. The deductions which are drawn from the values so obtained, in conjunction with other data already available, lead to certain conclusions as to the heats of formation both in the solid and ionic state which are of much wider interest and are dealt with in the next section.

In two former communications* there was developed a theory with reference to the ascertainment of the relative sizes of ions which was based upon a consideration of various physical data relating to KCl and NaCl. In the present paper the necessary data are given for extending the results to LiCl. In the former papers an empirical linear relationship was found between the solution volumes calculated from density measurements and the ionic volumes deduced from conductivity and viscosity measurements, which is now extended to LiCl. In the present paper a new empirical relation will be found between the ionic volumes and the reciprocals of the effective molecular freezing-point depressions* of the three salts in question. These two sets of empirical relations are found to be capable of simple theoretical interpretations, and to yield in combination interesting information as to the relative volumes and densities of the ions and of the ionic nuclei.

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* I shall have necessity to refer from time to time to these papers, and will do so under the short names "Ionic Sizes I" and "Ionic Sizes II." An abstract of the former is to be found in 'Roy. Soc. Proc.,' 1905, p. 563, but the references herein given are to the full paper, which was published, with some additions, in the 'Zeit. für Phys. Chem.,' 1905, vol. 53, p. 257. The second paper was published in 'Phil. Trans.,' 1906, A, vol. 206, p. 101. For the understanding of the later sections of the present communication it is necessary that the reader should have the second paper before him.

The three salts above mentioned are compounded of some of the most compressible of the elements, and are therefore admirably suited for a consideration of volume changes in relation to heats of formation.

Now that we are coming to regard an atom as being itself composed of hundreds of more minute bodies (which we will designate as corpuscles, in order to adopt a neutral term) there is no *a priori* improbability in the theory of the compressibility of atoms. We shall therefore express our results in terms of this hypothesis, to which they appear to give considerable support.

In order to correlate changes of atomic volume with heats of formation, it was necessary to consider a wider group of compounds of the same class as the three salts above mentioned. For this purpose certain available data exist within a sufficient area to enable a useful generalisation to be made. These data lead us to a new law relating to the heats of formation of the solid and liquid compounds formed from the elements and radicles of the substances considered, which may be enunciated as follows:—

The heat of formation due to the combination in the liquid or solid state of any of the electro-positive elements with any of the electro-negative elements or radicles is approximately equal to the sum of certain calorific constants of the two elements or radicles, together with 0·875 δV, where δV is the change of atomic volume produced by the combination.

This leads us to the conception of the internal energy of an atom as the sum of the kinetic energy of the corpuscles and of their potential energy under their mutually attractive forces. On this view, the heat component, 0·875 δV, represents the change in the internal energy of the atoms due to their volume changes on combination.

The heats of ionisation of KCl, NaCl, and LiCl are apparently irregular and have not hitherto been regarded as periodic functions of the atomic volumes. The application of the factor 0·875 to the contraction of volume of the nuclei will be found to show the heats of ionisation as periodic functions.

It further appears probable that we can bring the heat of ionisation into complete subordination to the same general law as that above enunciated for the solid and liquid compounds of the same class.

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* In a former paper (Ionic Sizes II, p. 142) I used this expression to indicate the so-called molecular depression Δ/N divided by $(1+a)$, where a is the ionisation coefficient. The effective molecular depression of the freezing point may be shortly indicated by the letters E.M.D., so that the E.M.D. is $\Delta/N\,(1+a)$.

2. *Components of Heats of Formation of Solid, Liquid, and Ionic Molecules.*—Sufficiently complete data are available for most of the compounds of H, K, Na, and Li, with the radicles Cl, Br, I, NO_3, IO_3, to enable us to arrive at a generalisation within this limited area as to the relation between heats of formation and atomic volumes. The values of the atomic volumes of the elements in the uncombined state are indicated by the letter V, and are set out at the foot of the table. The values are those given by Mendeléeff, with the exception of those for K, Na, and Li, for which the values are those given by Richards based on his own density determinations.* The atomic volumes of the positive elements of each compound are set out in the column headed V_1, and those of the negative radicles in the column headed V_2. The values given for the compound radicles, such as NO_3, are merely the sums of the atomic volumes of their components. The column headed V_1+V_2 gives the sums of the atomic volumes of the elements in each compound. Under ρ are given the densities of the solid and liquid compounds, and under W their atomic weights. The quotient W/ρ is therefore the actual molecular volume of each compound. The difference V_1+V_2-W/ρ is the contraction of volume for each molecule which takes place on combination, and is set out in the column δV. The actual heats of formation in kilogramme-calories from Thomsen's data are given in the column headed H.F. It will now be seen from the table that each heat of formation is the sum of three quantities, viz., a part which is proportional to the total contraction, and is expressed by $0{\cdot}875\ \delta V$, and a remainder which is the sum of two components H_1 and H_2, which have approximately the same value for each radicle in every combination. To split the additive components into two parts H_1 and H_2 we require a definite starting-point, which is wanting. It is obvious, however, from the heats of formation of HCl, HNO_3, and HIO_3 that the calorific constant for the hydrogen atom is comparatively small. If we place it at 1 then the calorific constants for the other radicles are those given under "Values of H" at the foot of the table. If the value of H_1 for hydrogen were 3 instead of 1 we have only to diminish the heat components H_2 for each of the negative radicles by 2, and increase the heat components H_1 for the positive radicles by the same amount. It must, therefore, be understood that the value of 1 for the heat component for hydrogen is arbitrary, but it makes no difference to the additive scheme. The result is that all the heats of formation may be approximately expressed as

$$\Sigma = 0{\cdot}875\ \delta V + H_1 + H_2.$$

The separate components are set out in three columns of the table and the

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* 'Journ. Amer. Chem. Soc.,' 1909, vol. 31, p. 156.

Table I.—Components of Heats of Formation of Solid and Liquid Compounds.

	V_1.	V_2.	V_1+V_2.	ρ.	W.	W/ρ.	δV.	$0·875\,\delta V$.	H_1.	H_2.	Σ.	H.F.	Diff.
HCl	12·0	27	39·0	0·85	36·5	43·0	−4	−3·5	1·0	24·3	21·8	22·0	−0·2
KCl	45·5	27	72·5	1·87	74·6	40·0	32·5	28·4	53·0	24·3	105·7	105·6	+0·1
NaCl	23·7	27	50·7	2·04	58·5	28·7	22·0	19·3	54·2	24·3	97·8	97·7	+0·1
LiCl	13·1	27	40·1	1·575	42·5	27·0	13·1	11·5	58·0	24·3	93·8	93·8	±
HNO_3	12·0	49	61·0	1·53	63·0	41·2	19·8	17·3	1·0	26·0	44·3	41·5	+2·8
KNO_3	45·5	49	94·5	2·06	101·2	49·1	45·4	39·7	53·0	26·0	118·7	119·5	−0·8
$NaNO_3$	23·7	49	72·7	2·25	85·0	37·8	34·9	30·5	54·2	26·0	110·7	111·3	−0·6
$LiNO_3$	13·1	49	62·1	2·33	69·0	29·6	32·5	28·4	58·0	26·0	112·4	111·6	+0·8
HIO_3	12·0	62	74·0	4·63	176·0	38·0	36·0	31·5	1·0	25·0	57·5	58·0	−0·5
KIO_3	45·5	62	107·5	3·98	214·2	53·8	53·7	47·0	53·0	25·0	125·0	124·5	+0·5
KBr	45·5	26	71·5	2·7	119·1	44·1	27·4	24·0	53·0	17·7	94·7	95·3	−0·6
NaBr	23·7	26	49·7	3·08	103·0	33·4	16·3	14·3	54·2	17·7	86·2	85·8	+0·4
KI	45·5	26	71·5	3·07	166·2	54·1	17·4	15·2	53·0	9·5	77·7	80·1	−2·4
NaI	23·7	26	49·7	3·45	150·0	43·5	6·2	5·4	54·2	9·5	69·1	69·1	±

	H.	K.	Na.	Li.	NO_3.	IO_3.	Cl.	Br.	I.
Values of V	12	45·5	23·7	13·1	49·0	62	27·0	26·0	26·0
Values of H	1	53·0	54·2	58·0	26·0	25	24·3	17·7	9·5

$$\Sigma = 0·875\,\delta V + H_1 + H_2.$$

sum in the column headed Σ. The column headed "Diff." shows the differences between the observed and calculated heats of formation.

The principle which is involved in the relationship which thus comes to light is probably capable of wider application, but data for extending the generalisation are very difficult to obtain. At the suggestion of Prof. Sir J. Larmor data have been collected for another group. They are set out in Table II. The errors between observed and calculated values are about twice as great as in the first group, but the heats of formation of the bivalent salts are also about twice as great. Within the area of both these groups we can say that the heat of formation due to the combination of one of the electro-positive atoms with one of the electro-negative atoms or radicles is the sum of three components, two of which are constants belonging to the several combining atoms or radicles, and the other of which is approximately $0{\cdot}875\,\delta V$, where δV is the contraction which takes place on combination.

The last component possesses great interest in connection with the theory of the compressibility of the atom. It appears probable that the component represents the change of internal energy due to the contraction of the atoms on combination.

Let us conceive the corpuscles of a free or uncombined atom as vibrating in a certain maximum space with a maximum average amplitude at a given temperature, the volume of the atom being determined by an equilibrium between attractive forces, which tend to approximate the corpuscles and to reduce the volume, and the energy of motion of the corpuscles, which tends to increase the volume. If we suppose such an atom to contract or to be compressed isothermally, the internal kinetic energy would be diminished, owing to the reduction of the amplitude of the corpuscular vibrations with reduction of volume, and the internal potential energy would be diminished, owing to the approximation of mutually attractive corpuscles. This reduction of internal energy appears to be expressed by, or at all events included in, the component $0{\cdot}875\,\delta V$, which would thus represent the heat so developed. This, in the case of KCl, amounts to more than a quarter of the total heat of formation, and in the case of the nitrates and iodates to a still larger fraction. We have spoken of a reduction of internal energy due to compression, but it must be observed that in the cases of HCl and ZnI_2, to which the law also extends, there is an increase of atomic volume on combination, and a resulting increase of internal energy.

We may now apply the result obtained as regards δV to the consideration of the heats of formation of ions. The compression of the atoms in the ionic state is even greater than in the solid state, as we may see from the values of

Table II.—Components of Heats of Formation of Solid Salts with Bivalent Bases.

	V_1.	$2V_2$.	V_1+2V_2.	ρ.	W.	W/ρ.	δV.	$\frac{7}{8}\delta V$.	H_1.	$2H_2$.	Σ.	H.F.	Diff.
$CaCl_2$	25 ·3	54	79 ·3	2 ·205	111 ·1	50 ·4	28 ·9	25 ·3	93 ·2	48 ·6	167 ·1	169 ·8	−2 ·7
$SrCl_2$	35 ·0	54	89 ·0	2 ·96	158 ·6	53 ·6	35 ·4	31 ·0	102 ·7	48 ·6	182 ·3	184 ·6	−2 ·3
$BaCl_2$	36 ·0	54	90 ·0	3 ·75	208 ·4	55 ·5	34 ·5	30 ·2	118 ·1	48 ·6	196 ·9	194 ·7	+2 ·2
$ZnCl_2$	9 ·5	54	63 ·5	2 ·753	136 ·4	49 ·5	14 ·0	12 ·3	38 ·0	48 ·6	98 ·9	97 ·2	+1 ·7
$CdCl_2$	13 ·0	54	67 ·0	3 ·655	183 ·4	50 ·2	16 ·8	14 ·7	31 ·2	48 ·6	94 ·5	93 ·2	+1 ·3
$CaBr_2$	25 ·3	52	77 ·3	4 ·794	200 ·1	60 ·3	17 ·0	14 ·9	93 ·2	35 ·4	143 ·5	140 ·9	+2 ·6
$SrBr_2$	35 ·0	52	87 ·0	3 ·985	247 ·6	62 ·1	24 ·9	21 ·8	102 ·7	35 ·4	159 ·9	157 ·7	+2 ·2
$BaBr_2$	36 ·0	52	88 ·0	4 ·23	297 ·4	70 ·3	17 ·7	15 ·5	118 ·1	35 ·4	169 ·0	170 ·0	−1 ·0
$ZnBr_2$	9 ·5	52	61 ·5	3 ·643	225 ·4	61 ·9	−0 ·4	−0 ·4	38 ·0	35 ·4	73 ·0	75 ·9	−2 ·9
$CdBr_2$	13 ·0	52	65 ·0	4 ·794	272 ·4	56 ·8	8 ·2	7 ·2	31 ·2	35 ·4	73 ·8	75 ·2	−1 ·4
ZnI_2..............	9 ·5	52	61 ·5	4 ·696	319 ·4	68 ·0	−6 ·5	−5 ·7	38 ·0	19 ·0	51 ·3	49 ·2	+2 ·1
CdI_2..............	13 ·0	52	65 ·0	5 ·644	366 ·4	64 ·9	0 ·1	0 ·1	31 ·2	19 ·0	50 ·3	48 ·8	+1 ·5

	Ca.	Sr.	Ba.	Zn.	Cd.	Cl.	Br.	I.
Values of H........................	93 ·2	102 ·7	118 ·1	38	31 ·2	24 ·3	17 ·7	9 ·5

$$\Sigma = \tfrac{7}{8}\delta V + H_1 + 2H_2.$$

δV set out below, which are deduced from the values of EV_0 obtained in Section 7.

	KCl.	NaCl.	LiCl.
Solid state, δV	32·5	22·0	13·1
Ionic state, δV	42·7	29·9	18·7

This is probably due to the superiority of the attractive forces which come into play as between the atoms and water, over the mutual forces between the atoms themselves of the solid solute.

The heats of formation of the solid salts, which are in the order of their atomic weights and volumes, being

KCl.	NaCl.	LiCl.
105·6	97·7	93·8

may be regarded as periodic functions.

On the other hand, the heats of ionisation appear to be irregular, being

101·2 96·5 102·2

It seems clear that the heat component due to atomic compression, which probably expresses the reduction of the internal energy of the atom due to the approximation of its corpuscles, should equally be a component of the heat of ionisation. The application of this consideration at once regularises the heats of ionisation.

	KCl.	NaCl.	LiCl.
Heats of ionisation	101·2	96·5	102·2
0·875 δV	37·4	26·2	16·4
Remainder	63·8	70·3	85·8

If $n = 9, 13, 21$, respectively be the numbers of water molecules combined with the solute (see the last section of this paper), and if we attribute to each molecule of combined water a calorific constant 1·85, we may express the heats of ionisation of the three salts by one formula

$$\text{Heat of ionisation} = 0{\cdot}875\,\delta V + 1{\cdot}85\,n + 46{\cdot}6.$$

It will be noticed that in this scheme the idiosyncrasies of the ions K, Na, Li have disappeared except so far as they affect contraction and water combination, no place having been found for their individual calorific constants H_1 and H_2, as to whose values it may be observed that they are so near to one another that they would not throw out by much the constant 46·6, which is included in the above scheme. Moreover, we have not included anything for the water contraction, except that its effect will be approximately brought out in the water calorific constant 1·85 per molecule. We will, therefore, now include all these elements in the scheme and see how the matter stands.

It appears highly probable that the heat component 0·875 δV, which represents the heat correlated with the contraction of the atoms, must also be applied to the contraction of the water. We can work out this contraction from the figures in the last section of the paper, which give

	KCl.	NaCl.	LiCl.
Total contraction δV of combined water......	3·518	5·457	4·880
And therefore for water, 0·875 δV	3·1	4·8	4·3

If we now include this item and also the calorific constants for the atoms, we find that on this basis the calorific constant for the water molecule works out at 1·3 (a figure which agrees approximately with the figures later deduced from the hydration of H_2SO_4), and there is a negative heat component which is approximately 29.

The whole scheme is then as follows :—

Table III.—Components of Heats of Ionisation.

	KCl.	NaCl.	LiCl.
0·875 δV (solute)	37·4	26·2	16·4
0·875 δV (water)	3·1	4·8	4·3
$H_1 + H_2$....................	77·3	78·5	82·3
1·3 n	11·7	16·9	27·6
Negative constant	−29·0	−29·0	−29·0
Sum of components ...	100·5	97·4	101·6
Heats of ionisation......	101·2	96·5	102·2
Difference	−0·7	+0·9	−0·6

Thus within the narrow margin shown by the differences the three heats of ionisation are given by

$$\Sigma\, 0{\cdot}875\, \delta V + \Sigma H + 1{\cdot}3\, n - 29.$$

On the whole, this must be regarded as the most probable scheme, and it has the advantage of bringing heats of formation of solid salts and ionised salts under one general law, when it is noted that the number 1·3 for the water molecule is a calorific constant of precisely the same kind as those belonging to the atoms and radicles.

It should be noted that the appearance of a negative constant is necessary, since the heats of ionisation are the sum of not only positive but negative elements.

It might be thought, at first sight, that to attribute a calorific constant to water molecules when they enter into combination in different numbers with different salts would be inconsistent with the well-known generalisation of Thomsen that the addition of each successive molecule of water adds a diminished quantity to the heat of formation. This, however, is not necessarily the case. First, it must be noted that we have only dealt with the limiting case of practically complete ionisation. Then, too, the contraction δV for each successive molecule of water is probably less.

It must also be remembered that Thomsen's figures refer to the heat per molecule of water added, and that only a portion of this enters into actual combination. We may give an example of this by considering the heats due to the mixture of H_2SO_4 with 1, 2, and 3 molecules of water. The researches of Mendeléeff, Pickering and others make it probable that up to two molecules of water nearly the whole of the added water is in chemical combination with the acid. The heat of dilution law which our general law yields if the whole water enters into combination is

$$F = 0{\cdot}875\ \delta V + nH_w,$$

where n is the number of molecules of water in combination with the solute, and δV the contraction which takes place on addition of the water. We may take Mendeléeff's density data* and Thomsen's data for the heats of dilution F. Mendeléeff's figures are for 15° C. and Thomsen's data for 18° C., which will produce a small inaccuracy.

Table IV.—Heats of Dilution of $H_2SO_4 + nH_2O$,

n.	ρ_{15}.	δV.	F.	$0{\cdot}875\,\delta V$.	$F - 0{\cdot}875\,\delta V$.	H_w.
0	1·8372					
1	1·7772	6·08	6·38	5·32	1·06	1·06
2	1·6500	8·16	9·42	7·14	2·28	1·14
3	1·5501	9·33	11·14	8·16	2·98	0·99

The last column shows the value of H_w which results from these figures on the assumption that the whole of the water is in combination with the acid. Thus up to $n = 2$ a value for H_w is yielded which is very nearly equal to the value 1·3 deduced from the ions of the three salts above mentioned. For three molecules the value of H_w falls off and still more as n increases, indicating that after the addition of two molecules of water, further additions only combine in part with the acid, a proportion of the water remaining as free water. In fact, the low values we get for H_w for the first two molecules of water may indicate that the whole of the water is not combined.

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* 'Principles of Chemistry,' Ed. 1905, vol. 2, p. 271.

We may now summarise some of the results which this investigation tends to establish within the area which has been considered.

(1) The heats of formation both of the solid, liquid, and ionic molecules considered have a component $0·875\,\delta V$ depending upon the total contraction of the combining atoms and radicles and water molecules.

(2) These heats of formation have also components which are calorific constants for the various atoms and radicles and also for the combining water molecules.

(3) The theory of the compressibility of the atom is in accord with these results and interprets our component $0·875\,\delta V$ as the heat evolution due to the reduction of the internal energy of the atom owing to the contraction due to combination.

(4) In the process of ionisation, the ionic nuclei, which are reduced in size, may be regarded as in a state of chemical combination with their attached water molecules, such combination yielding the energy required for dissociating the solid salt, together with a surplus.

3. *Experimental Work. Density and Viscosity of LiCl Solutions.*—To determine solution volumes in dilute solutions with sufficient accuracy for our purpose, densities accurate within a unit in the fifth place of decimals are required. For the present determinations were used a pair of pyknometers of the kind formerly described* of a capacity of 300 to 400 c.c. The most important determinations were made in duplicate and in some cases repeated. The figures are given in the following table :—

Table V.—Density Determinations of LiCl Solutions at 18° C.

m.	First series.	Second series.		Value taken.	V_s.
		Pyk. I.	Pyk. II.		
1	1·02286	1·022928	1·022922	1·02292	0·4294
$\frac{1}{2}$	1·01100			1·01100	0·4190
$\frac{1}{4}$	1·00494			1·00494	0·4087
$\frac{1}{8}$	1·00184			1·00184	0·4011
$\frac{1}{16}$	1·00028	1·000254 1·000257	1·000250 1·000255	1·000265	0·396
$\frac{1}{32}$	0·99950	0·999473 0·999466	0·999466 0·999457	0·99947	0·3926
$\frac{1}{64}$	0·99909			0·99909	

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* 'Trans. Chem. Soc.,' 1908, vol. 93, p. 679.

The values of the solution volume V_s calculated from the densities are given in the last column.

The viscosities of the LiCl solutions were determined with a viscosimeter of the type described in a former paper.* The observations were made in duplicate. The results are given in the following table, together with the equivalent viscosity increment. The viscosity of water at 18° C. is taken as the unit:—

Table VI.—Viscosities of LiCl Solutions at 18° C.

m.	η.	$\frac{\eta-1}{m}$.
1	1·1497	0·1497
$\frac{1}{2}$	1·0761	0·1522
$\frac{1}{4}$	1·0392	0·1568
$\frac{1}{8}$	1·0207	0·1656
$\frac{1}{16}$	1·0116	0·1856
$\frac{1}{32}$	1·0071	0·2272
$\frac{1}{64}$	1·0045	

From $m = 1$ to $m = 1/16$ a straight line law expresses the viscosity with good accuracy for interpolation as follows:—

$$\eta = 1{\cdot}0024 + 0{\cdot}1473\, m.$$

Beyond $m = 1/16$, the values at the points required for our calculations can be obtained by setting out the values of the equivalent viscosity increment upon a curve. The required values are as follows:—

m.	η.
0·0005	1·0002
0·001	1·0003
0·005	1·0014
0·01	1·0026
0·05	1·0095
0·10	1·0170

Grüneisen† determined the viscosity of LiCl solutions, but only at two points. His values, compared with those above, are as follows:—

m.	Values above.	Grüneisen.
1·0	1·1497	1·1498
0·1	1·0171	1·0161

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* "Ionic Sizes I," p. 304.

† 'Wiss. Abhand. der Phys. Tech. Reichsanstalt,' 1905, vol. 4, p. 246.

It is considered that the present values, based on a complete series, are preferable to those of Grüneisen.

4. *The Empirical Volume Equations.*—For the method of deduction of the ionic volumes reference must be made to the former papers. For obtaining the true values of α from the Van't Hoff equation, the following values of C are taken:—

	KCl.	NaCl.	LiCl.
C =	0·505	0·520	0·531

The ionisations which result from the use of these constants may be compared with those which result from taking the ordinary $\alpha = \lambda/\lambda_\infty$ at the concentration $m = 0{\cdot}001$. The values resulting from these values of C are:—

	KCl.	NaCl.	LiCl.
α =	0·9765	0·9753	0·9744

whilst the other values are

	KCl.	NaCl.	LiCl.
λ/λ_∞ =	0·9788	0·9771	0·9761

The latter values, which neglect variation of viscosity and ionic size, are, as they should be, somewhat higher than our values, but the relative ionisations remain about the same.

As a slightly different value of the constant for NaCl is now taken, the figures for NaCl have been recalculated. The required empirical relation between solution volumes and ionic volumes for LiCl, calculated as in the former papers, is

$$V_s = 0{\cdot}5112 - 0{\cdot}004094\, I_V.$$

It is useful as a test of our values for the ionic volumes to see what values for the densities are obtained from the ionic volumes. Density may be expressed in terms of solution volumes as

$$\rho = \rho_0 + \frac{m}{1000}(E - \rho_0 E V_s),$$

where $\rho_0 = 0{\cdot}99866$, the density of water at 18° C., and $E = 42{\cdot}48$, the molecular weight of LiCl.* Substituting these values and expressing V_s in terms of I_V, we have for the density

$$\rho = 0{\cdot}99866 + m\,(0{\cdot}02079 + 0{\cdot}0001737\, I_V).$$

It will be noticed that there are in this equation only two independent constants, the values of I_V having been obtained entirely without reference to the densities. The calculated and observed densities are set out in the table.

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* In this paper the old molecular weights are taken, as Kohlrausch's values of λ were ased on these figures.

Table VII.—Observed and Calculated Densities of LiCl at 18° C.

m.	I_V.	ρ observed.	ρ calculated.	Difference.
1	19·11	1·02292	1·02277	−15
$\frac{1}{2}$	22·51	1·01100	1·01101	+ 1
$\frac{1}{4}$	25·05	1·00494	1·00494	±
$\frac{1}{8}$	26·84	1·00184	1·00184	±
$\frac{1}{16}$	28·06	1·00026	1·00026	±
$\frac{1}{32}$	28·86	0·99947	0·99947	±
$\frac{1}{64}$	29·39	0·99909	0·99907	− 2

We may repeat an observation made in a former paper. The ionic volumes are obtained only from the sizes of the ions, being based on conductivity measurements which take no account of un-ionised molecules. The fact that the densities can be accurately calculated from the ionic volumes indicates that the un-ionised molecules follow approximately the same volume law as if they consisted of two ions joined together. It is important to bear this in mind, as it enables us to use the ionic volumes for deriving the total amount of water combination both for ionised and un-ionised molecules.

The complete results from this and the former papers are as follows :—

Hydration Numbers B.

$$B_{KCl} = 3{\cdot}33, \qquad B_{NaCl} = 3{\cdot}2, \qquad B_{LiCl} = 3{\cdot}08,$$

$$B_{Cl} = 3{\cdot}5, \qquad B_K = 3{\cdot}16, \qquad B_{Na} = 2{\cdot}75, \qquad B_{Li} = 2{\cdot}26.$$

Empirical Relations between I_V and V_s.

KCl .... $V_s = 0{\cdot}408 - 0{\cdot}0075\, I_V$.

NaCl .... $V_s = 0{\cdot}3647 - 0{\cdot}00655\, I_V$.

LiCl .... $V_s = 0{\cdot}5112 - 0{\cdot}004094\, I_V$.

The molecular solution volumes are obtained by multiplication by the equivalent weights, which are (old atomic weights)—

	KCl.	NaCl.	LiCl
E =	74·6	58·5	42·48.

These lead to the empirical volume relations in the form in which they are required for use :—

KCl .... $EV_s = 30{\cdot}44 - 0{\cdot}560\, I^V$.

NaCl .... $EV_s = 21{\cdot}33 - 0{\cdot}383\, I_V$.

LiCl .... $EV_s = 21{\cdot}72 - 0{\cdot}1739\, I_V$.

These equations are of the form

$$EV_s = a - bI_V,$$

the constants a and b for each salt being as shown.

5. *Comparative Values of Ionic Volumes.*—In the former paper* the application of Stokes' theorem, on the assumption that the ions were spherical and had approximately the same coefficient of friction, led to the relationship $r = G/v\eta$, where r is the radius of the ion, v its true mobility, η the viscosity of the solution, and G was taken as a constant for monovalent ions and the value unity was given to it. The examination of this relationship over a larger group soon showed that this could only be regarded as a first approximation, and it became clear that variations of ionic shape and of friction had to be reckoned with, so that G must be regarded as varying from ion to ion. Moreover, in seeking for a factor for reducing the arbitrary ionic volume units to the ordinary volume unit, it already appeared† that a slightly different factor would have to be taken for KCl and NaCl. The factor γ which was used for converting ionic volume units to litres was obtained from a consideration of the relative viscosities and was taken to be 0·32 for KCl and 0·30 for NaCl. A much greater difference in the factor γ was found to be necessary when LiCl was brought into consideration, and the deduction of the factor from the viscosities, in any case a difficult matter, was found to be still more difficult. It therefore became necessary to find a better method for evaluating γ. Now in working from the factors deduced from the viscosities it was found‡ that, both in the case of KCl and NaCl, we were led to the result that the effective molecular freezing-point depression, over a certain range of concentration, came out as a constant when reckoned upon the free water in the solution, that is, after deducting from the total water the amount of combined water calculated from the ionic volumes. In the present paper this is taken as the starting point for the determination of γ. A new and more convenient empirical relation between ionic volume and freezing-point depression enables the factors to be worked out upon a systematic basis. This relation is of the form

$$\frac{1}{D} = p - qN(I_V - K),$$

where D is the effective molecular freezing-point depression, N is the number of gramme-molecules of solute per 1000 grm. water, I_V is the ionic volume reckoned in the old units, and K is the volume of the ionic nuclei in the same units, p and q being constants. By the use of this empirical relation in combination with that between ionic volume and solution volume it is possible to evaluate γ and to obtain the volumes both of the ions and of the ionic nuclei. One theoretical defect in this process must not be overlooked.

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* "Ionic Sizes II," p. 155.

† "Ionic Sizes II," p. 139.

‡ "Ionic Sizes II," p. 149.

This is that we are using ionic volumes based on conductivities measured at 18° C. as applicable to the solutions in the neighbourhood of the freezing point. To make our deductions strictly accurate, the ionic volumes should be based on conductivities also measured in the neighbourhood of the freezing point. But no sufficiently accurate data of this kind are in existence. The general character of the deductions of this paper will not be seriously modified by this defect.

It should be remembered that though a different factor γ is required for each salt to make the ionic volumes derived from the mobilities comparable as between the different salts, yet for any given salt the ionic volumes are strictly comparable through a certain range of concentration. Each set of ionic volumes, calculated as in the former papers from conductivity and viscosity data, must be considered as being given in its own arbitrary unit, the factor γ in each case reducing the arbitrary unit to ordinary units.

It should be noted that though we use the separate radions r_1 and r_2 of the positive and negative ions to arrive at the joint ionic volume of the solute $(r_1^3+r_2^3)\times 10^6$, our factor γ, being applied to the joint volumes, cannot be used to obtain the absolute values of the radions. These are not wanted for our present purpose, but to indicate that r_1 and r_2 require different factors to reduce them to absolute values it is better to term r_1 and r_2 the "mobility radions."

6. *Analytical Treatment of the Empirical Equations.*—Before we are in a position to evaluate the required constants of the new empirical relation

$$\frac{1}{D} = p - qN(I_V - K),$$

it is necessary to consider its physical meaning in combination with that of the other empirical relation

$$EV_s = a - bI_V.$$

It will be convenient at this stage to collect together the symbols used in a tabulated form for reference.

Symbols Used.

V_s = Solution volume of 1 grm. of solute.
V_0 = Volume which 1 grm. of solute occupies in solution.
E = Weight of 1 gramme-molecule of solute.
ϵ = Weight of 1 gramme-molecule of water.
ρ_u = Density of free or uncombined water.
ρ_c = Average density of water which is in combination with the solute.
ϵ/ρ_u = Volume of 1 gramme-molecule of free water.
ϵ/ρ_c = Volume of 1 gramme-molecule of combined water.

$\zeta = \epsilon\left(\frac{1}{\rho_u} - \frac{1}{\rho_c}\right)$ = contraction which 1 gramme-molecule of water undergoes in combination.

n = Number of molecules of water combined with 1 molecule of solute.

I_V = Ionic volume of a gramme-molecule of solute with its combined water.

γ = Factor necessary to reduce ionic volume units to litres, so that

$1000\,\gamma I_V$ = Volume of 1 gramme-molecule of hydrated solute in cubic centimetres.

α = Coefficient of ionisation.

Δ = Freezing-point depression in degrees Centigrade of a solution containing N gramme-molecules of solute to 1000 grm. water.

$D = \frac{\Delta}{N(1+\alpha)}$ = effective molecular depression of the freezing point.

K = Volume of 1 gramme-molecule of solute in ionic units, so that

$EV_0 = 1000\,\gamma K$.

w = Weight of uncombined water in 1000 grm. of total water.

N = Molecules of solute to 1000 grm. water.

We found formerly* that the E.M.D., when reckoned upon the free water of the solution only, came out as a constant. The E.M.D. is

$$D = \frac{\Delta}{N(1+\alpha)},$$

when this is reckoned upon the total water. We shall still keep D to express this fraction. The fact that the E.M.D. when reckoned upon the free water is a constant will then be expressed by

$$\frac{Dw}{1000} = F, \qquad (1)$$

where F is a constant, and is equal to 1·86, or whatever number we decide to adopt as best for the limiting value of the E.M.D.

The volume of water combined with 1 gramme-molecule of solute is $I_V - K$, where K is the volume of the ionic nuclei. If γ is the factor required to reduce ionic volumes to litres and ρ_c is the average density of the combined water, the weight (in grammes) of water combined with 1 gramme-molecule of solute is

$$1000\,\gamma\rho_c(I_V - K), \quad \text{so that} \quad w = 1000 - 1000\,N\gamma\rho_c(I_V - K).$$

Hence equation (1) may be expressed as

$$\frac{1}{D} = \frac{1}{F} - \frac{N\gamma\rho_c}{F}(I_V - K). \qquad (2)$$

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* "Ionic Sizes II," p. 149.

Our empirical relation is

$$\frac{1}{\mathrm{D}} = p - q\mathrm{N}(\mathrm{I_V} - \mathrm{K}). \tag{3}$$

Hence we have $p = 1/\mathrm{F}$ and $q = \gamma\rho_c/\mathrm{F}$,

and we thus get for the required value of γ

$$\gamma = \frac{q}{p\rho_c}. \tag{4}$$

But there is still an unknown quantity ρ_c, the density of the combined water, involved in this equation and an unknown quantity K is required for the deduction of p and q. We can obtain these by a concurrent consideration of the other set of empirical relations

$$\mathrm{EV}_s = a - b\mathrm{I_V}. \tag{5}$$

To interpret this equation we must remember that EV_s, the solution volume of a molecule of solute, is the volume which the molecule of solute occupies in solution less the contraction of the water which combines with the solute, that is to say,

$$\mathrm{EV}_s = \mathrm{EV}_0 - n\zeta, \tag{6}$$

where V_0 is the volume which 1 grm. of solute occupies in the solution, ζ is the average contraction which 1 molecule of water undergoes in combination with the solute, and n is the number of molecules of water combined with 1 molecule of solute.

It must further be noted that the volume of 1 molecule of the hydrated solute, that is of 1 molecule of the ions and partly ionised molecules, is the volume which 1 molecule of solute occupies in solution *plus* the volume of the combined water, that is to say,

$$1000\gamma\mathrm{I_V} = \mathrm{EV}_0 + \frac{n\epsilon}{\rho_c}, \tag{7}$$

where ϵ is the weight of a molecule of water.

By elimination of n between (6) and (7) and noting that

$$\frac{\zeta\rho_c}{\epsilon} = \frac{\rho_c}{\rho_u} - 1,$$

where ρ_u is the density of the uncombined water, we get

$$\mathrm{EV}_s = \mathrm{EV}_0\frac{\rho_c}{\rho_u} - 1000\gamma\left(\frac{\rho_c}{\rho_u} - 1\right)\mathrm{I_V}. \tag{8}$$

If we assume that at high dilutions ρ_c, the density of the combined water, and ρ_u, the density of the free water, are constants we may now compare our empirical equation (5) with equation (8), and equate coefficients. But it is likely that there may be a change in the density both of the free water and the combined water in passing from high to low dilutions, and this limitation must, therefore, be borne in mind. Equating coefficients we get

$$a = \mathrm{EV}_0 \frac{\rho_c}{\rho_u}, \tag{9}$$

$$b = 1000\gamma\left(\frac{\rho_c}{\rho_u} - 1\right). \tag{10}$$

Now K is the volume of the ionic nuclei in the same units as $\mathrm{I_V}$, and, therefore, $\mathrm{EV}_0 = 1000\gamma\mathrm{K}$. Hence from (9) and (10) we get

$$\mathrm{K} = \frac{a}{b} \cdot \frac{\rho_c - \rho_u}{\rho_c}. \tag{11}$$

From (4) and (10), by eliminating γ, we get

$$b = \frac{1000q}{p\rho_c}\left(\frac{\rho_c - \rho_u}{\rho_u}\right).$$

Whence also

$$\mathrm{K} = \frac{pa\rho_u}{1000q}. \tag{12}$$

K is thus expressed in terms of the constants of the empirical equations.

Also from (4) and (10) by eliminating ρ_c we get

$$\gamma = \frac{q}{p\rho_u} - \frac{b}{1000}, \tag{13}$$

and from (4), (9), and (13)

$$\mathrm{EV}_0 = a - \frac{pab\rho_u}{1000q}. \tag{14}$$

EV_0 is thus expressed in terms of the constants. By reason of (12) the last equation may be written in the interesting form

$$\mathrm{EV}_0 = a - b\mathrm{K}. \tag{15}$$

Finally, the density of the combined water is given by (9), which may be written

$$\rho_c = \frac{a\rho_u}{\mathrm{EV}_0}. \tag{16}$$

For the simple calculation of q from the experimental data we obtain from equations (3) and (12) the relation

$$q = \frac{1}{\mathrm{I_V}}\left[\frac{1}{\mathrm{N}}\left(p - \frac{1}{\mathrm{D}}\right) + \frac{pa\rho_u}{1000}\right]. \tag{17}$$

It will be noticed that we have treated ρ_c and ρ_u as if our conductivity data were taken at the same temperature as the freezing-point data. This may in some equations produce an error of nearly two parts per thousand, but the error produced on the value of q is inappreciable. It should also be noticed that by treating ρ_c and ρ_u as constants in the region of high dilution we bring out K as a constant. This would introduce a small error at low dilution, as K must probably be larger at such dilutions, owing to the reduced pressure on the nuclei when the ions are smaller and the water combination is less. We have also neglected the difference in the value of K as between 0° C. and 18° C.

7. *The Empirical Relation between Freezing-Point Depression and Ionic Volume, and Deduction of Constants.*—We are now in a position to obtain the empirical relations between freezing-point depression and ionic volume for the three salts under consideration. Let us first take the identical set of figures set out in the former paper* for KCl. These were there shown to lead to the relation $D = 1{\cdot}86 + c\delta I_V$ within the limits of experimental error. They equally lead to the new relation

$$\frac{1}{D} = p - qN(I_V - K)$$

within the same limits. The choice of the new relation instead of the old one is determined by the fact that it admits of a precise theoretical interpretation as was shown in the preceding section.

In the following table, in the first, second, third, and fourth columns are set out the same figures as were formerly given for KCl. The values for the molecular depression of the freezing point Δ/N are those given by Jahn.†

The figures given for the calculated values of $1/D$ are obtained by taking

$$p = 0{\cdot}534, \qquad q = 0{\cdot}0138, \qquad K = 1{\cdot}2.$$

Table VIII.—Empirical Relation between Freezing-point Depression and Ionic Volume for KCl.

N.	I_V.	α.	Δ/N.	$\frac{1}{D} = \frac{N(1+\alpha)}{\Delta}$.	$I_V - K$.	$qN(I_V - K)$.	1/D calc.	Diff.
0·3395	5·297	0·727	3·337	0·518	4·097	0·0192	0·515	−3
0·3377			3·344	0·515		0·0191	0·515	±
0·259	5·568	0·749	3·37	0·519	4·368	0·0156	0·518	−1
0·201	5·794	0·769	3·385	0·523	4·594	0·0127	0·521	−2
0·151	6·021	0·790	3·41	0·524	4·821	0·0121	0·522	−2
0·100	6·289	0·819	3·472	0·524	5·089	0·0070	0·527	+3
			3·457	0·526			0·527	+1
0·076	6·443	0·837	3·485	0·527	5·243	0·0055	0·529	+2
0·054	6·626	0·863	3·50	0·532	5·426	0·0038	0·530	−2
0·0378	6·733	0·878	3·55	0·529	5·533	0·0029	0·531	+2
0·02552	6·881	0·896	3·547	0·535	5·681	0·0020	0·532	−3
0·02527			3·562	0·532		0·0020	0·532	±

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* "Ionic Sizes II," p. 143.

† 'Zeit. Phys. Chem.,' 1904, vol. 50, p. 136.

If we look at the values of 1/D derived from Jahn's duplicate experimental values for Δ/N, we see that the differences on our calculated values of 1/D are of the same order as Jahn's experimental differences, and we may therefore say without doubt that the new empirical relation is established within the limits of experimental error. At the lowest concentration, which is the most important for determining the limiting value of 1/D, Jahn's results give a difference of 0·003 on 1/D. But such experimental differences at low concentration cannot be avoided, and, as a consequence, we find that Jahn's figures for the three salts KCl, NaCl, LiCl, yield three different values for the constant p, which should theoretically be the same for each.

It seems clear that these differences in the value of p, which is the limiting value of 1/D at infinite dilution, can only be due to experimental errors, and we shall, therefore, take a fixed value for p which is the same in all three cases. The reciprocal of the value 0·534 which is yielded by the above figures is 1·872. This is a higher value than that which is usually accepted. Bedford's figures* seem to be the most recent and the most reliable. The highest figures which he obtained for the molecular depression of the freezing point with KCl solutions were 3·736 and 3·734, corresponding to effective molecular depressions of 1·868 and 1·867. We shall assume as the basis of our calculation 1·867 as the right figure, instead of 1·874. This gives the value of our constant $p = 1/1{\cdot}867 = 0{\cdot}5355$, instead of 0·534. Taking this value of p we might deduce from Jahn's figures for each salt a value of q for the salt which would be the mean value yielded by all the figures. Since, however, the probable error in the value of Δ/N given by any particular observation is inversely proportional to N^2 we shall deduce the value of q from the mean of the two highest concentrations given in each case by Jahn. As we are dealing with a straight line law this will be likely to give us the best values.

The figures which Jahn gives for these concentrations are as follows:—

Table IX.—Jahn's Values for Depression of Freezing Point.

	N.	Δ.	Δ/N.
KCl	0·3395	1·1320	3·337
	0·3377	1·1292	3·344
NaCl	0·3022	1·0279	3·401
	0·2998	1·0207	3·404
LiCl	0·2938	1·0370	3·530
	0·2939	1·0389	3·535

Using the values of the hydration numbers B and ionisation constants C before given we arrive at the following figures by taking the mean of each pair of observations.

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* 'Roy. Soc. Proc.,' 1910, A, vol. 83, p. 454.

	N.	$h = \frac{55\cdot506}{N}$.*	Log *h*.	α.	I_V.
KCl	0·3386	163·9	2·21458	0·7244	5·298
NaCl	0·3010	184·4	2·26576	0·7257	12·105
LiCl.........	0·29385	188·9	2·27623	0·7211	24·546

* *h* is the number of molecules of water per gramme-molecule of solute.

From these figures, taking $p = 0\cdot5355$, we arrive at the values for q and K which are given in the following table:—

Table X.—Values of the Constants q and K.

	Δ/N.	1/D.	q.	K.
KCl	3·3405	0·5162	0·01383	1·176
NaCl ...	3·4025	0·5072	0·00871	1·310
LiCl......	3·5325	0·4872	0·00717	1·620

The values of q are easily obtained by the use of equation (17), taking the given data and putting $p = 0\cdot5355$, $\rho_u = 0\cdot99866$, and taking the value of a furnished by the empirical volume relation.

Our complete table of the constants of the empirical equations and of the values deduced from them by means of equations (4), (12), (13), (14), (15), and (16) is as follows:—

Table XI.—Constants Derived from the Empirical Equations.

	a.	b.	p.	q.	K.	EV_0.	ρ_c.	1000 γ.
KCl......	30·44	0·560	0·5355	0·01383	1·176	29·78	1·0208	25·30
NaCl ...	21·33	0·383	0·5355	0·00871	1·310	20·83	1·0225	15·92
LiCl ...	21·72	0·1739	0·5355	0·00717	1·620	21·44	1·0117	13·25

8. *Application to Ionic Volumes at Infinite Dilution.*—We are now in a position to complete the data required, in order to arrive at the analysis of the ionic heats which is contained in Section 2 of this paper. For this purpose it is only necessary to apply the figures obtained to deduce approximately the number of molecules of water combined with each pair of ions. The total volume of a gramme-molecule of ions in cubic centimetres is $1000\,\gamma I_V$. From this we must deduct the volume of the ionic nuclei to get the volume of the combined water, and multiply by the mean density of this water to get

the weight. Hence the weight of water combined with a gramme-molecule of ions of the solute at infinite dilution is

$$\rho_c(1000\gamma I_V - EV_0).$$

Using the data given above the weights of combined water deduced are as follows:—

KCl.	NaCl.	LiCl.
157·1	233·9	384·6

which expressed in molecules of water are

	KCl.	NaCl.	LiCl.
$n =$	8·9	13	21·3

These numbers should be integers at infinite dilution, and taking the nearest integers we get for the molecules of water combined with the pairs of ions at infinite dilution,

KCl.	NaCl.	LiCl.
9	13	21

It has, of course, been observed that our analysis has not given us any means of separating the volumes of the several ions, or of the amounts of their separate water combination. Our factor γ is a factor which deals with the sum of the ionic volumes, and our quantity EV_0 is the sum of the volumes of the nuclei. But having regard to the mobilities of K and Cl and to the transference numbers, we may reasonably conclude that the K and Cl ions are of nearly equal size.

If we took the Cl ion to be combined with five molecules of water, we should have for the water combination of the other ions

	K.	Na.	Li.
$n =$	4	8	16

This is a very attractive looking series and there is something to be said for it. Let us compare certain corresponding properties of the K and Cl atoms and ions—

	K.	Cl.
Mobilities	64·6	65·4
Atomic volumes	45·0	27·0
Compressibilities	31·5	95·0

Now the joint contracted volume in the ionic state is 30. This is 5/12ths of the original joint volume 72. If the compressibilities were equal and the internal pressures in the ions equal, the respective contracted volumes would be

$$18{\cdot}7 + 11{\cdot}3 = 30;$$

but, allowing for the difference in compressibility, they might be more nearly

$$25+5 = 30.$$

This would allow the Cl ion to have one more molecule of water than the K ion, and yet have a less volume and greater mobility.

Unfortunately, Washburn's transference experiments in order to determine the relative hydration* indicate that the numbers should be the other way, and that the K ion has one more molecule than the Cl ion, in which case the numbers for the separate ions yielded by our figures would be

	Cl.	K.	Na.	Li.
$n =$	4	5	9	17

Whether Washburn's method, which rests on the mixture with the solution of a non-electrolyte, such as sucrose or raffinose, is completely reliable is possibly open to some question. If the Cl ion be taken to be combined with four molecules of water, the figures which his experiments yield are

	Cl.	K.	Na.	Li.
$n =$	4	5·4	8·4	13·0

which may be compared with those above. His figures are only relative, as his method does not yield absolute results, and the figures are for concentrations of about 1·2 normal instead of infinite dilution.

The division of the combined water between the separated ions is a matter of great interest, but fortunately it is quite unnecessary for the main purpose of this paper, which was developed in the second section.

In conclusion, we may again refer to the fact that the precise figures depend, according to this method, on what is to be taken as the true value of the freezing-point constant. If the low value 1·845 be taken instead of the value 1·867, the figures come out as follows:—

	KCl.	NaCl.	LiCl.
$n =$	11	16	24

but the general results of the second section of this paper are not affected thereby, though the value of the calorific constant 1·3 for the water molecule in combination would be slightly altered.

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* 'Technological Quarterly,' 1908, vol. 21, p. 288.